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(54) **Dental article containing light-curable paste**

**Zahnärztlicher Artikel mit lichterhärtbarer Paste**

**Produit dentaire contenant une pâte polymérisable à l'effet d'une lumière**

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(56) References cited:  
**US-A- 4 117 596                      US-A- 4 204 325  
US-A- 4 226 593**

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## Description

[0001] Curable pastes useful as restorative materials and adhesives for orthodontic brackets are known. However, use of such pastes often requires painstaking measurement of components and mixing by the dental practitioner. Further, the practitioner must carefully determine the minimum amount of paste necessary for bonding in order to avoid excess adhesive around the bracket, which would require further time consuming removal in order to eliminate an undesirable site for plaque accumulation. Furthermore, many known pastes have the disadvantage of having to be activated outside the mouth, before application, thereby reducing available working time inside the mouth; once the paste was activated, the practitioner had little time to work the paste, e.g., into a suitable restoration element. U. S. Patent No. 4,204,325, which forms the basis for the preamble of Claim 1, discloses an orthodontic bracket having a curable paste layer applied thereto, which is covered by a releasable film. After removing the film, and prior to placement of the bracket on the tooth, the paste layer is activated by surface application of a curing agent. Since activation occurs outside the mouth, the practitioner is given little time to position the bracket at the precise location desired on the tooth surface.

[0002] Accordingly, the present invention is a dental tape comprising a light-curable, non-toxic paste layered between two cover sheets, at least one of which releasably adheres to the paste.

[0003] Fig. 1 is an end elevational view of the tape of the present invention.

[0004] A tape of the present invention is useful in restorative applications, such as cosmetic veneers, veneers to mask severely stained teeth, cervical erosion repair, a desensitizing cover for sensitive teeth, a fiber reinforced splint or lay-up tape for chemical crowns and denture molds, a matrix strip to be formed, cured, and then filled with a dental restorative, or an orthodontic bracket adhesive tape.

[0005] Light-curable, non-toxic pastes useful in accordance with the present invention preferably contain a photoinitiator and a filler dispersed in a resin. Useful resins are hardenable, organic compounds having sufficient strength, hydrolytic stability, and non-toxicity to render them suitable for use in the mouth. Examples of such resins include acrylate, methacrylate, urethane, and epoxy resins, such as disclosed in U.S. Pat. Nos. 3,066,112, 3,539,533, 3,629,187, 3,709,866, 3,751,399, 3,766,132, 3,860,556, 4,002,669, 4,115,346, 4,259,117, 4,292,029, 4,306,190, 4,327,014, 4,379,695, 4,387,240, and 4,404,150.

Mixtures and derivatives of such resins are also useful. Preferably, the resin is a mixture of diglycidylmethacrylate of Bisphenol A ("Bis-GMA") and triethyleneglycol dimethacrylate ("TEGDMA"). Useful photoinitiators are non-toxic compounds, such as ketone or alpha-diketone compounds, alone or in combination with suitable amines, peroxides, sulfur compounds, phosphorus compounds, or other compounds capable of reacting with or being sensitized by the ketone or alpha-diketone compounds to effect polymerization of the resin. Preferred photoinitiators include a mixture of di-camphorquinone and dimethylaminophenethanol ("DMAPE"), and photoinitiator systems such as disclosed in European Pat. Application No. 0290133. Suitable fillers for oral use are well known, such as disclosed in U.S. Pat. Nos. 4,895,251 and 4,435,160. Preferred fillers include quartz, radiopaque glass, and non-vitreous microparticles as disclosed in U.S. Pat. No. 4,503,169. The microparticles are particularly advantageous in pastes intended for anterior restorations since they provide a cured composite paste having a low visual opacity. Other preferred fillers include low hardness minerals such as kaolinite, mica, pyrophyllite, and talc.

[0006] The paste is preferably prepared in the absence of light by first combining the resin and photoinitiator and then adding the filler. In some applications, absence of occluded air from the paste is desirable, e.g., in matrix composites and bracket adhesives. Accordingly, the paste is preferably mixed under partial vacuum as well.

[0007] The paste contains a filler and optional pigment to produce varying degrees of opacity as desired. Optionally, the paste is fiber or fiber scrim reinforced for applications such as splinting. Useful fiber types include glasses, such as electrical grade glass, and ceramics. Useful scrims have various yarn types, identified by the number of filaments per yarn, the number of yarns per 2.54 cms (inch) in both warp (machine) and fill (transverse) directions, and the weave style.

[0008] Optionally, the paste includes suitable adjuvants such as accelerators, inhibitors, stabilizers, pigments, dyes, viscosity modifiers, extending or reinforcing fillers, surface tension depressants and wetting aids, or anti-oxidants. Particularly useful optional ingredients include colloidal silica thickeners, which help provide an optimum viscosity for the paste, and may permit higher amounts of filler loading needed for particular applications.

[0009] Amounts of components used in the paste vary depending on particular ingredients used as well as the intended application. Generally the resin/filler ratio is adjusted to provide a sufficient consistency to the paste to permit easy handling and prevent slump. Generally, more heavily loaded pastes provide more visually opaque cured products. The amount of photoinitiator used is generally an amount sufficient to cure the resin after a brief exposure to a curing light. For general applications, the paste preferably comprises 10-40% resin, 60-90% filler, and 0.1-5.0%, more preferably 0.1-1.0%, photoinitiator. The thickness of the paste layer is adjustable by the skilled artisan depending on specific applications, with preferred thickness varying between about 0.2 and 1.3 mm.

[0010] The tape of the present invention contains the paste sandwiched between two cover sheets, at least one of which removably adheres to the paste. As shown in Fig. 1, dental tape 1 contains paste 2 sandwiched between flexible

cover sheets 3. Removably adhering cover sheets are preferably "hand hard" (i.e., resilient) films made of polyester, fluorinated polymers such as polytetrafluoroethylene, or olefin polymers such as polypropylene or polyethylene. More preferably, the removably adhering cover sheet has a low-adhesion backsize coating applied on the surface contacting the paste for ease of removal of the tape. Such low-adhesion backsize coatings include silicone coatings and polytetrafluoroethylene coatings, which are well known to those skilled in the art. Preferably, the thickness of the removably adhering cover sheet is between about 0.00635 and 0.0127 mm. In applications where both cover sheets are removed before curing the paste, e.g., bracket adhesives, both cover sheets of the tape removably adhere to the paste.

[0011] For use in restorative applications and as matrix tapes, one of the cover sheets preferably remains on the paste until it is cured. Accordingly, the remaining cover sheet is preferably transparent to light of the desired curing wavelength to allow optimum curing of the paste. For matrix tape applications, the transparent cover sheet is preferably a "dead-soft" or "hand-soft" (i.e., non-resilient) film, such as polyvinylidene chloride. Other useful hand-soft films will be readily apparent to those of ordinary skill in the art. The thickness of the transparent cover sheet preferably varies between about 0.0127 and 0.508 mm, more preferably between about 0.0178 and 0.0254 mm. Thin cover sheets are particularly useful when the transparent sheet must fit between adjacent teeth, such as in splinting and matrix banding.

[0012] Methods of making the tape of the present invention include pattern coating, knife coating, reverse roll coating, nip roll coating, and other methods that will be apparent to those in the art.

[0013] For an orthodontic bracket adhesive, disposed in a tape the paste preferably contains 10-70% resin and 30-90% filler by weight of the paste. Precise amounts, determinable by the skilled artisan, vary depending on the particular components used as well as the bracket composition. In an adhesive tape, the paste has a preferable thickness between 0.245 and 0.508 mm. The filler preferably has a Mohs hardness less than about 4, more preferably less than about 3. These preferred values for Mohs hardness ensure a filler that is less hard than either natural tooth enamel or the typical abrasive materials used for adhesive removal, thus facilitating removal of the adhesive after the orthodontic bracket is removed at the termination of treatment while minimizing enamel damage. When used as a bracket adhesive, the consistency of the paste is preferably adjusted to provide the desired mechanical retention of the paste on the bracket as well as to allow good mesh penetration and flow around the screen wires of both 60 and 100 mesh screen bases of orthodontic brackets.

[0014] The dental tape of the present invention is also useful as a matrix band in place of metal matrix bands used in many Class II restorations. Utilizing the dental tape of the present invention allows for more precise shaping of the tape to the original contour of the tooth and for proper spacing in contact areas. Following placement of the matrix band around a tooth that was drilled to remove part of the side of the tooth, the paste covering the hole in the side of the tooth is cured using a curing light. The drilled area now enclosed by the remaining tooth structure and the cured paste is filled with a suitable restorative material, which is then cured, the entire restoration providing an integrally formed, matrix-tape restoration. After curing of the restoration, the transparent cover film is removed to reveal a fully cured and lustrous surface. Surface lustre may be adjusted by using cover films with various finishes, e.g., matte. Since the matrix tape can be made very thin, it can easily be wedged between adjoining teeth. The practitioner can also immediately determine the contact area between adjacent teeth and shape or compress the uncured matrix layer accordingly. For matrix tape applications, the resin amount is preferably between about 10-50%, more preferably 10-15%, based on the weight of the paste. The preferred amount of filler in matrix tape applications is about 50-90%, more preferably 85-90%, based on the weight of the paste. For matrix tape applications, the thickness of the paste layer is preferably between about 0.127 and 0.254 mm. Since the matrix band is wound around the tooth surface, a minimal thickness is desired to allow ease of placement between the teeth.

[0015] The dental tape of the present invention is also useful as a veneer to replace lost, damaged, or discolored tooth enamel. When used as a veneer, the paste layer has a thickness between about 0.25 and 0.5 mm. For veneers, the resin amount is preferably between about 10-20%, more preferably 10-15%, based on the weight of the paste. The preferred amount of filler in veneers is about 80-90%, more preferably 85-90%, based on the weight of the paste. In repairing cervical erosion of teeth, several applications of tape may be necessary, depending on the thickness of the paste layer used and the depth of erosion.

[0016] In restorative applications, translucency of the cured paste is often preferred for cosmetic reasons. However, for masking severely stained teeth, a more opaque paste is preferred. Visual opacity is controlled by matching the refractive indices of the resin and the filler. The closer the refractive indices, the more translucent the cured paste. Of course, opacity is also affected by the thickness of the cured paste. That is, a cured paste may be translucent at a given thickness, but become progressively more opaque as thickness increases. Furthermore, visual opacity is reduced by removal of occluded air from the paste, e.g., by mixing the paste under partial vacuum.

[0017] Again, depending on ultimate use, the paste is preferably radiopaque (i.e., opaque to x-rays) or radiolucent (i.e., translucent to x-rays). The amount of radiopacity can vary and is measurable by known methods, such as disclosed in the aforesaid U.S. Pat. No. 4,503,169.

[0018] Optionally, the paste used in accordance with the present invention contains reinforcing fibers such as glass or ceramic fibers. Preferably, the fibers have an index of refraction closely matching the cured resin to maintain the

desired translucency, for example, in veneer or matrix tape applications. In an orthodontic bracket adhesive tape a fiber scrim is preferably imbedded in the adhesive layer.

[0019] To more fully describe the present invention, the following non-limiting examples are provided. All parts and percentages in the examples are by weight unless indicated otherwise.

#### EXAMPLE 1

[0020] A series of light-curable pastes containing a resin system and a filler system are mixed in a light-excluding mixer (Double Planetary Ross Mixer Model LDM, Charles Ross & Son, N.Y.) and formed into tapes for orthodontic adhesives. The resin system is a 50/50 blend of Bis-GMA and TEGDMA, combined with 0.25% camphorquinone and 0.5% dimethylaminophenethanol, based on the weight of the resin. The filler system formulations along with pertinent test data are shown in Table 1. The colloidal silica used is a hydrophilic, amorphous, fumed colloidal silica having a 50 m<sup>2</sup>/g particle surface area (available from Degussa Corp. under the name Aerosil™ QX-50). The ZrO<sub>2</sub>/SiO<sub>2</sub> filler is prepared according to Example 6 in the aforesaid U.S. Pat. No. 4,503,169.

TABLE 1

SAMPLE NUMBER	FILLER SYSTEM		% FILLER LOADING IN PASTE	COMPRESSIVE STRENGTH (p.s.i.)	DIAMETRAL TENSILE STRENGTH (p.s.i.)	CONSISTENCY (mm)
	WEIGHT% COLLOIDAL SILICA	WEIGHT % ZrO <sub>2</sub> /SiO <sub>2</sub> FILLER				
1	0	80.00	80.0	57120	11613	27.78
2	2.0	78.00	80.0	57365	11332	28.58
3	2.8	77.20	80.0	58262	11487	31.75
4	4.0	76.00	80.0	58042	12176	39.69
5	4.5	77.80	82.3	62101	12049	25.4
6	8.0	72.00	80.0	62000	12467	46.04
7	10.7	73.20	83.9	66246	13526	36.51
8	13.2	74.80	88.0	64394	13664	28.58
9	21.97	65.93	87.9	68538	14030	28.58
10	32.0	48.00	80.0	66132	13312	43.66
11	40.0	40.00	80.0	67179	12641	39.69
12	48.0	32.00	80.0	69234	12804	26.99
13	52.5	22.50	75.0	68576	10468	32.54
14	56.08	14.02	70.1	71148	9831	42.07
15	62.3	0	62.3	68357	9546	42.86

[0021] The adhesives are formed into tapes by rolling or pressing the pastes between low adhesion cover sheets. Two types of low adhesion cover sheets are used: (1) a low-density polyethylene-coated paper with a silicone release agent (Polyslick™, General Electric) applied to the polyethylene coat and a high density polyethylene coat on the backside of the paper to prevent curling, and (2) a clay-filled kraft paper coated with a silicone release agent (Silicone Premium, General Electric). The tapes are slit into narrow widths to correspond to the bracket width. The bracket used is an American Orthodontics, Bracket No. 095-007, 100 mesh, stainless steel brazed, central. Segments are then cut to fit the bracket screen, one cover sheet is removed and the adhesive is pressed onto the bracket screen. The remaining cover sheet is removed and the bracket is pressed onto an acid etched bovine tooth. To cure the paste, an ESPE "Elipar" dental curing light is directed around the periphery of the bracket for 20 seconds. A 0.3675 mm adhesive thickness provides good adhesion, requiring little or no clean-up of excess adhesive.

[0022] To determine compressive strength and diametral tensile strength, a sample of the uncured paste is placed in a 4.06 mm I.D. glass tube capped with silicone plugs in each end of the tube. The tube is placed in a test rig pressurized

with air at 0.28 MPa. The test rig contains two ESPE "Elipar" dental curing lights aimed at opposing sides of the tube and mounted on a turntable which enables the lights to be rotated around the tube in a 180° arc. The light guide of each curing light is spaced 3 mm from the tube wall. While operating both curing lights simultaneously and oscillating them continuously around the tube, the tube is exposed to four 20 second curing cycles. The tube is then removed from the test rig, placed on a pair of spaced rollers, and rotated under a 110 watt "Ritter" dental operator light at a distance of 0.6 meters for one hour. The cured sample is removed from the tube and sliced into cylinders with a diamond saw. For compressive strength testing, an 8.23 mm long cylinder is employed, and for diametral tensile strength testing, a 2.21 mm long cylinder is employed. The cylinders are stored in 37° C distilled water for 24 hours, then tested according to ADA Specification Nos. 8 and 27.

- [0023] Consistency is measured as the spread of 0.5 ml of paste sandwiched between two 10.16 x 10.16 cm glass plates under a 907.2 g weight. A quantity of 0.50 ml paste is delivered onto the bottom plate, then the top plate and 907.2 g weight are added. The combined mass of the top plate and the 907.2 g weight = 1027 ± 10 g. After 2 min., the spread (diameter) of the paste is measured to the nearest 0.794 mm, and 3 readings are averaged.

## EXAMPLE 2

- [0024] Composite matrix tapes and veneer tapes are prepared using the same resin system as in EXAMPLE 1 combined with various filler loadings. The filler used is a combination of 80% ZrO<sub>2</sub>/SiO<sub>2</sub> (prepared as in EXAMPLE 1 of the aforesaid U.S. Pat. No. 4,503,169) and 20% colloidal silica as used in EXAMPLE 1. Four paste samples are prepared, with the following total filler loadings: Paste 1 - 80% loading; Paste 2 - 83.5% loading; Paste 3 - 85.1% loading; and Paste 4 - 86.7% loading.

- [0025] Tapes are prepared using each of the four sample pastes sandwiched between a low adhesion cover sheet as described in EXAMPLE 1 and a transparent cover sheet of polyester film having a thickness of 0.0127 mm. A paste layer of 0.1225 - 0.245 mm thickness is obtained in each tape by rolling the sandwich with a glass jar or pressing the sandwich between glass plates. Ease of release of the paste layer from the low adhesive cover sheet is facilitated as filler loading increases.

## EXAMPLE 3

- [0026] A more highly loaded paste than in the previous examples is prepared. The filler system used is the same as EXAMPLE 1, but with 15% colloidal silica and 85% ZrO<sub>2</sub>/SiO<sub>2</sub> filler. The resin system used is the same as in EXAMPLE 1. Total filler loading is 88%. The paste is found to provide a further improvement in release. Handling properties and resistance to slump are also improved. A matrix tape using this paste is prepared as in EXAMPLE 2 having a paste thickness of 0.245 mm and a polyvinylidene chloride cover film having a thickness of 0.1715 mm. The matrix tape is used for a Class II restorative filling in an extracted human tooth. A hole is cut in the tooth removing part of a side of the tooth and part of the crown. The tape is cut to a length that slightly overlaps itself when wound around the tooth and to a width of 1.0 mm. Paste is removed from the tape leaving an amount sufficient to cover and slightly overlap the hole in the side of the tooth. The tape is wrapped around the tooth such that the paste remaining on the tape covers the hole in the side of the tooth. After placement around the tooth, the paste is cured by directing the hand held curing light described in EXAMPLE 1 over the area covered by the paste for about 20 seconds. The tooth is then filled with two successive layers of the paste used to make the matrix tape, each layer being cured by exposure to the curing light for about 30 seconds. The tape is easily placed and performs well while the tooth is filled. After the final layer of paste is cured, the tape is peeled away from the restoration. A lustrous surface finish and good contacts are obtained.

## EXAMPLE 4

- [0027] Paste formulations used to prepare matrix tapes as in EXAMPLE 2 are evaluated as veneers. Veneers are placed on bovine teeth and are easily shaped and tapered towards the incisal edge. After curing and removal of the transparent cover sheet, the veneer surface is completely cured and lustrous, requiring no polishing.

## EXAMPLE 5

- [0028] Human teeth exhibiting cervical erosion are treated with tapes prepared as in EXAMPLE 2. Several applications are required to fill some eroded areas, however placement is very rapid and an excellent surface requiring no polishing is produced.

# Claims

1. A dental tape (1) comprising a non-toxic (2) paste layered between two cover sheets (3), at least one of which releasably adheres to the paste (2), characterised in that the paste (2) is light-curable.
2. The tape (1) of claim 1 wherein at least one of the cover sheets (3) is a hand-soft, transparent film.
3. The tape (1) of any preceding claim wherein the releasably adhering cover sheet (3) is a hand-hard film that is opaque to light having a wavelength capable of curing the paste.
4. The tape (1) of any preceding claim wherein at least one of the cover sheets (3) releasably adheres to the paste (2) through a low-adhesion backsize coating.
5. The tape (1) of any preceding claim wherein the paste (2) is visually translucent after curing.
6. The tape (1) of any preceding claim wherein the paste (2) further comprises fibers that have an index of refraction the same as the resin after curing.
7. The tape (1) of any preceding claim wherein the paste (2) is radiopaque after curing.

## Patentansprüche

1. Zahnärztliches Band (1), umfassend eine nichttoxische Paste (2), die schichtförmig zwischen zwei Deckfolien (3) angeordnet, von denen mindestens eine an der Paste (2) ablösbar adhärert, dadurch gekennzeichnet, daß die Paste (2) lichthärtbar ist.
2. Band (1) nach Anspruch 1, bei welchem mindestens eine der Deckfolien (3) eine handweiche, transparente Feinfolie ist.
3. Band (1) nach einem der vorgenannten Ansprüche, bei welchem die adhärierende, ablösbare Deckfolie (3) eine handharte Feinfolie ist, die gegenüber Licht mit einer solchen Wellenlänge undurchlässig ist, die zum Härten der Paste in der Lage ist.
4. Band (1) nach einem der vorgenannten Ansprüche, bei welchem mindestens eine der Deckfolien (3) an der Paste (2) über eine klebschwache Rückseitenbeschichtung ablösbar adhärert.
5. Band (1) nach einem der vorgenannten Ansprüche, bei welchem die Paste (2) nach dem Härten visuell durchscheinend ist.
6. Band (1) nach einem der vorgenannten Ansprüche, bei welchem die Paste (2) ferner Fasern aufweist, die eine Brechzahl haben, die gleich derjenigen des Harzes nach dem Härten ist.
7. Band (1) nach einem der vorgenannten Ansprüche, bei welchem die Paste (2) nach dem Härten strahlenundurchlässig ist.

## Revendications

1. Ruban dentaire 1) comprenant une pâte non toxique (2) disposée en couche entre deux feuilles de couverture (3) dont au moins une adhère de façon détachable à la pâte (2), caractérisé en ce que la pâte (2) est photopolymérisable.
2. Ruban (1) selon la revendication 1, dans lequel au moins une des feuilles de couverture (3) est un film transparent mou à la main.
3. Ruban (1) selon une quelconque des revendications précédentes, dans lequel la feuille de couverture (3) qui adhère de façon détachable est un film dur à la main qui est opaque à une lumière ayant une longueur d'onde capable de polymériser la pâte.

4. Ruban (1) selon une quelconque des revendications précédentes, dans lequel au moins une des feuilles de couverture (3) adhère de façon détachable à la pâte (2) par l'intermédiaire d'un revêtement d'enduction d'envers de faible adhérence.

5 5. Ruban (1) selon une quelconque des revendications précédentes, dans lequel la pâte (2) est visuellement translucide après polymérisation.

6. Ruban (1) selon une quelconque des revendications précédentes, dans lequel la pâte (2) comprend en outre des fibres qui ont un indice de réfraction semblable à celui de la résine après polymérisation.

10 7. Ruban (1) selon une quelconque des revendications précédentes, dans lequel la pâte (2) est radio-opaque après polymérisation.

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FIG. 1

